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(54) **Silicone pressure sensitive adhesive compositions**

(57) This invention provides pressure sensitive adhesive compositions which are obtainable by a method comprising reacting a mixture of at least one polydiorganosiloxane, at least one silicone resin copolymer, at least one silanol condensation catalyst, and at least one solvent or plasticizer having a boiling point of at least 200°C., to form a reaction product and then adding an organic peroxide or azo compound to the resultant reaction product. The silicone pressure sensitive adhesives of this invention are useful in preparing articles such as pressure sensitive tapes, labels emblems and other decorative or informational signs.

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Description

This invention provides silicon pressure sensitive adhesive compositions obtainable by reacting a mixture comprising a polydiorganosiloxane, a silicone resin copolymer, a condensation catalyst, and at least one solvent or plasticizer having a boiling point of at least 200°C. to form a reaction product, and then adding an organic peroxide or azo compound to the reaction product.

Silicone pressure sensitive adhesives are typically produced by either blending or condensing together a silicone resin and a silicone polymer. These types of silicone pressure sensitive adhesives are claimed in U.S. Patents 2,736,721, 2,814,601, 2,857,356 and 3,528,940.

Silicone pressure sensitive adhesives which are produced by adding an amine or a salt of an amine to the silicone resin-silicone polymer blend have been disclosed, for example, in Great Britain Patent Publication 998232. Silicone pressure sensitive adhesives are also disclosed which comprise a resin, a polydiorganosiloxane fluid and a condensation catalyst; namely, a metal salt of a carboxylic acid in U.S. Patent 4,831,070.

European Patent Publication 0459292 provides a silicone pressure sensitive adhesive composition comprising a mixture of two different pressure sensitive adhesive compositions containing resin and polymer blends.

U.S. Patent 5,248,739 teaches a silicone pressure sensitive adhesive composition produced by mixing together a silicone resin and a polydiorganosiloxane polymer and that these compositions can further comprise an organic peroxide as a crosslinking agent when the polydiorganosiloxane polymer does not contain unsaturated groups.

Great Britain Patent Publication 2,301,829 discloses silicone pressure sensitive adhesive compositions comprising 100 parts of an organopolysiloxane having a viscosity of at least 500,000 mPa · s (cP) at 25°C., 60 to 300 parts of a silicone MQ resin and 20 to 2500 parts of a linear or cyclic volatile organosiloxane fluid having a boiling point in the range of 95 to 250°C. where the organo radicals of the silicone pressure sensitive adhesive composition are selected from C₁₋₁₃ organo radicals which are attached to silicon by carbon-silicon linkages and further discloses that the curing of the silicone pressure sensitive adhesive composition is by the use of a free-radical initiator; namely, an organic peroxide. Conventional peroxide curable silicone pressure sensitive adhesives are generally supplied at 55 to 60% solids by weight in an organic (typically aromatic) solvent diluent. This is done to lower the viscosity of the film forming product, making it easier to handle and apply evenly to a desired substrate. These solvents normally boil at 100 to 140°C., and they are removed prior to thermal activation by a peroxide initiator.

We have found the addition of a high boiling organic solvent or plasticizer to silicone pressure sensitive adhesive compositions can improve the performance of the adhesive.

Our invention claims silicone pressure sensitive adhesive compositions which are obtained by reacting a mixture comprising at least one polydiorganosiloxane, at least one silicone resin copolymer, at least one condensation catalyst and at least one solvent or plasticizer having a boiling point of at least 200°C. to form a reaction product, and then adding an organic peroxide or azo compound to the reaction product.

Silicone pressure sensitive adhesives compositions produced by our invention exhibit high tack while retaining good peel adhesion. It is an object of our invention to provide silicone pressure sensitive adhesive compositions that are produced by condensing a polydiorganosiloxane in the presence of a silicone resin. It is further an object of this invention to provide a silicone pressure sensitive adhesive composition having a high solids content or are solventless which maintain excellent adhesive properties at low viscosities. It is another object of this invention to provide silicone pressure sensitive adhesive compositions which are particularly suitable in adhesive tape constructions.

Our invention introduces a silicone pressure sensitive adhesive composition obtainable by a method comprising the steps of (I) reacting a mixture comprising: (A)(i) at least one hydroxyl-terminated polydiorganosiloxane having a viscosity of from 100 to 100,000,000 mm²/s at 25°C. or (ii) a mixture of (a) a hydroxyl-terminated polydiorganosiloxane and (b) a polydiorganosiloxane selected from (i) polydiorganosiloxanes terminated with monovalent hydrocarbon radicals free of aliphatic unsaturation or (ii) alkenyl-terminated polydiorganosiloxanes wherein said mixture has a viscosity of from 100 to 100,000,000 mm²/s at 25°C., (B) at least one soluble silicone resin essentially consisting of at least one R₃SiO_{1/2} unit and at least one SiO_{4/2} unit, wherein R is independently selected from a monovalent hydrocarbon or halo-hydrocarbon radical free of aliphatic unsaturation and having from 1 to 20 carbon atoms, an alkenyl radical or a hydroxyl radical wherein the molar ratio of R₃SiO_{1/2} units to SiO_{4/2} units is from 0.5:1 to 1.2:1, (C) at least one silanol condensation catalyst selected from liquid catalysts having a boiling point of less than 200°C. or catalysts which are solid at room temperature and (D) at least one solvent or plasticizer having a boiling point of at least 200°C. to form a reaction product, and (II) adding (E) an organic peroxide or azo compound to the reaction product of (I).

The hydroxyl-terminated polydiorganosiloxane of component (A) is a polydiorganosiloxane having the general formula HOR¹₂SiO(R¹₂SiO)_nSiR¹₂OH wherein each R¹ is independently selected from a monovalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms or an alkenyl radical. The monovalent hydrocarbon radicals free of aliphatic unsaturation include alkyl radicals exemplified by methyl, ethyl, propyl, pentyl, octyl, undecyl or octadecyl; cycloaliphatic radicals exemplified by cyclohexyl; aryl radicals exemplified by phenyl, tolyl, xyl, benzyl or 2-phenylethyl; and chlorinated hydrocarbon radicals exemplified by 3-chloropropyl and dichlorophenyl. Th alkenyl radicals

include vinyl, allyl, butenyl, hexenyl, cyclohexenyl and beta-cyclohexenylethyl. R^1 is selected from methyl, phenyl or vinyl. The hydroxyl-terminated polydiorganosiloxane of component (A) is a compound in which at least 50% of the R^1 radicals are methyl radicals.

The average value of subscript "a" above provides a viscosity at 25°C. of 100 mm²/s (100 centistokes) to 100,000,000 mm²/s (100,000,000 centistokes), the viscosity is a function of the R^1 radicals on the polymer. It is preferred that the average value of "a" is such that it provides an organopolysiloxane component (A) having a viscosity in the range of 1,000 to 50,000,000 mm²/s at 25°C., and it is more preferred that "a" has a value such that the viscosity of component (A) ranges from 2,000 to 500,000 mm²/s when measured at 25°C.

Specific examples of these polydiorganosiloxanes include; $\text{HOMe}_2\text{SiO}(\text{Me}_2\text{SiO})_a\text{SiMe}_2\text{OH}$, $\text{HOPh}_2\text{SiO}(\text{Me}_2\text{SiO})_{0.94a}(\text{Ph}_2\text{SiO})_{0.06a}\text{SiPh}_2\text{OH}$, $\text{HOMe}_2\text{SiO}(\text{Me}_2\text{SiO})_{0.95a}(\text{MeViSiO})_{0.05a}\text{SiMe}_2\text{OH}$, $\text{HOVi}_2\text{SiO}(\text{Me}_2\text{SiO})_{0.95a}(\text{MeViSiO})_{0.05a}\text{SiVi}_2\text{OH}$ or $\text{HOR}_2\text{SiO}(\text{Me}_2\text{SiO})_{0.88a}(\text{Ph}_2\text{SiO})_{0.12a}\text{SiR}_2\text{OH}$ wherein Me, Vi and Ph hereinafter denote methyl, vinyl and phenyl, respectively, and "a" is as defined above. Component (i) can also be a mixture of two or more different hydroxyl-terminated polydiorganosiloxanes.

Component (A) can also be (ii) a mixture of (a) a hydroxyl-terminated polydiorganosiloxane and (b) a polydiorganosiloxane selected from (i) polydiorganosiloxanes terminated with monovalent hydrocarbon radicals free of aliphatic unsaturation or (ii) alkenyl-terminated polydiorganosiloxanes wherein said mixture has a viscosity of from 100 to 100,000,000 mm²/s at 25°C. The hydroxyl-terminated polydiorganosiloxane is as described above including preferred embodiments thereof. The monovalent hydrocarbon radicals free of aliphatic unsaturation and the alkenyl radicals are as described above including preferred embodiments thereof.

Specific examples of polydiorganosiloxanes terminated with monovalent hydrocarbon radicals free of aliphatic unsaturation include; $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_a\text{SiMe}_3$, $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{0.95a}(\text{MeViSiO})_{0.05a}\text{SiMe}_3$, $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{0.5a}(\text{MePhSiO})_{0.5a}\text{SiMe}_3$, or $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{0.5a}(\text{Ph}_2\text{SiO})_{0.5a}\text{SiMe}_3$ wherein "a" has an average value as defined above.

Specific examples of polydiorganosiloxanes terminated with alkenyl radicals include; $\text{ViMe}_2\text{SiO}(\text{Me}_2\text{SiO})_a\text{SiMe}_2\text{Vi}$, $\text{ViMe}_2\text{SiO}(\text{Me}_2\text{SiO})_{0.95a}(\text{MePhSiO})_{0.05a}\text{SiMe}_2\text{Vi}$, $\text{ViMe}_2\text{SiO}(\text{Me}_2\text{SiO})_{0.98a}(\text{MeViSiO})_{0.02a}\text{SiMe}_2\text{Vi}$, $\text{PhMeViSiO}(\text{Me}_2\text{SiO})_a\text{SiPhMeVi}$, $\text{ViMe}_2\text{SiO}(\text{Me}_2\text{SiO})_{0.95a}(\text{Ph}_2\text{SiO})_{0.05a}\text{SiMe}_2\text{Vi}$, $\text{PhMeViSiO}(\text{Me}_2\text{SiO})_{0.8a}(\text{MePhSiO})_{0.1a}(\text{Ph}_2\text{SiO})_{0.1a}\text{SiPhMeVi}$ wherein "a" has an average value as defined above.

If component (A) is (ii) a mixture of (a) and (b) as defined above, the mixture of (a) and (b) is in weight ratios of (a):(b) of 1:99 to 99:1, is preferably from 90:10 to 10:90, and more preferred from 70:30 to 30:70.

In component (A), the molar sum of phenyl and vinyl radicals cannot exceed 30% of the silicon atoms. In addition, component (A) can comprise trace amounts of siloxane branching sites; namely, $\text{R}^1\text{SiO}_{3/2}$ units and $\text{SiO}_{4/2}$ units, provided that the component remains flowable. Component (A) is well known in the art and is prepared by known methods which need not be repeated herein.

The amount of component (A) in our compositions is from 30 parts to 50 parts by weight and, more preferable, from 37 to 47 parts by weight per 100 parts by weight of components (A)+(B).

Component (B) is at least one soluble silicone resin essentially consisting of at least one $\text{R}_3\text{SiO}_{1/2}$ unit (M unit) and at least one $\text{SiO}_{4/2}$ unit (Q unit), wherein R is independently selected from a monovalent hydrocarbon or halohydrocarbon radical having 1 to 20 carbon atoms, an alkenyl radical or a hydroxyl group, all of which are as described above. By the term "soluble", it is meant that the silicone resin (B) is dispersed in either a hydrocarbon liquid exemplified by benzene, toluene, xylene, heptane and the like or in a silicone liquid; namely, cyclic or linear polydiorganosiloxanes. The resin is soluble in component (A), delineated above. The silicone resin of component (B) is a soluble hydroxy-functional organopolysiloxane resin consisting of M units and Q units. In the hydroxyl functional organopolysiloxane resin, the $\text{R}_3\text{SiO}_{1/2}$ units are bonded to the $\text{SiO}_{4/2}$ units, each of the latter being bonded to at least one other $\text{SiO}_{4/2}$ unit. Some of the $\text{SiO}_{4/2}$ units are bonded to hydroxy radicals resulting in $\text{HOSiO}_{3/2}$ units, thereby accounting for the silicon-bonded hydroxyl content of the resin. In addition, the resin may contain a small amount of a low molecular weight material comprised of a neopentamer organopolysiloxane having the formula $(\text{R}_3\text{SiO})_4\text{Si}$. It is preferable that the hydroxy-content of the silicone resin or resin mixture as determined by ²⁹Si NMR (nuclear magnetic resonance) ranges from 1.0 to 5.0 wt% based on the resin solids content, and 1.5 to 3.5 wt%. However, resins having less than 1.0 wt% hydroxy can also be used in this invention.

In the formula for organopolysiloxane resin (B), the monovalent hydrocarbon radicals free of aliphatic unsaturation and the alkenyl radicals are as defined above, including preferred embodiments thereof. R is independently selected from methyl, phenyl, vinyl, hexenyl or hydroxyl. At least one-third, more preferably, all R radicals in the formula for component (B) are methyl radicals. Examples of preferred $\text{R}_3\text{SiO}_{1/2}$ units include $\text{Me}_3\text{SiO}_{1/2}$, $\text{ViMe}_2\text{SiO}_{1/2}$, $\text{PhMe}_2\text{SiO}_{1/2}$ or $\text{Ph}_2\text{MeSiO}_{1/2}$.

The molar ratio of $\text{R}_3\text{SiO}_{1/2}$ units to $\text{SiO}_{4/2}$ units is from 0.5:1 to 1.2:1. It is more preferred that the molar ratio of $\text{R}_3\text{SiO}_{1/2}$ units to $\text{SiO}_{4/2}$ units be from 0.6:1 to 1:1. The above M:Q molar ratios are easily obtained by ²⁹Si NMR. It is preferred that component (B) have a number average molecular weight (Mn) of 3,000 to 7,500 when measured by gel

permeation chromatography (GPC) calibrated against fractionated MQ resin standards. It is especially preferred that the molecular weight of Component (B) is from 3,500 to 6,000.

Component (B) is prepared by the silica hydrosol capping process of U.S. Patent 2,676,182, as modified by U.S. Patent 3,627,851 and U.S. Patent 3,772,247, wherein each patent teaches how to prepare soluble organopolysiloxanes that are useful in this invention. Further, component (B) is obtainable by the cohydrolysis of a trialkyl hydrolyzable silan and alkyl silicate as described in U.S. Patent 2,857,356.

The amount of component (B) in the compositions of our invention is from 50 to 70 parts by weight and, more preferably, from 53 to 63 parts by weight per 100 parts by weight of components (A)+(B). A preferred embodiment is the addition of a separate high-resin containing polymer-resin mixture to the initial resin-polymer mixture such that the resin content of the proportion of the combined resin and polymer mixture falls within the above limits.

Component (C) of this invention is at least one silanol condensation catalyst selected from liquid catalysts having a boiling point of less than 200°C. or catalysts which are solid at room temperature. The silanol condensation catalyst is selected from alkali metal hydroxides, alkali metal alkoxides, alkali metal carbonates, alkali metal silanates, amines, metal salts of amines, carboxylic acids or metal salts of carboxylic acids so long as the catalyst has the above essential properties. Component (C) is selected from amines, carboxylic acid salts of organic amines, quaternary ammonium salts, carboxylic acids and metal salts of carboxylic acids. Amines suitable for use as component (C) include primary amines exemplified by methylamine, ethylamine, propyl amine, hexylamine, butanolamine and butylamine; secondary amines exemplified by dimethylamine, diethylamine, diethanolamine, dipropylamine, dibutylamine, dihexylamine, ethylamine, imidazole and propylhexylamine; tertiary amines exemplified by trimethylamine, triethylamine, tripropylamine, tributylamine, trihexylamine, methyldipropylamine, tripropanolamine, pyridine, N-methylimidazole and methylpropylhexylamine. Carboxylic acid salts of organic amines suitable as component (C) are exemplified by diethylammonium acetate, butylammonium octoate and trimethylammonium laurate. Quaternary ammonium salts suitable as component (C) are exemplified by tetramethylammonium acetate, methylethyldibutylammonium chloride or dioctadecyldimethylammonium chloride. Carboxylic acids suitable as component (C) are exemplified by acetic acid, propanoic acid, butanoic acid, formic acid, stearic acid, tetradecanoic acid, hexadecanoic acid, dodecanoic acid, decanoic acid, 3,6-dioxahexanoic acid and 3,6,9-trioxadecanoic acid. Metal salts of carboxylic acids wherein the metal is selected from the group consisting of Li, Na, K, Ce and Ca are also suitable for use as component (C). The metal salts of carboxylic acids are exemplified by potassium formate and potassium acetate. Component (C) can also be a combination of two or more different condensation catalysts. It is preferred that component (C) is a tertiary amine.

The amount of component (C) in the compositions of our invention is from 0.01 to 20 parts by weight and, more preferably, from 0.1 to 5 parts by weight per 100 parts by weight of components (A)+(B).

Component (D) is at least one solvent or plasticizer having a boiling point of at least 200°C. The term "boiling point" for the purposes of this invention denotes the boiling point of a liquid at standard atmospheric pressure (101.3 kPa). The materials of component (D) are exemplified by aliphatic hydrocarbons including dodecane (bp of 216°C.), tridecane (bp of 234°C.), tetradecane (bp of 252°C.), 1-tetradecene (bp of 256°C.), pentadecane (bp of 266°C.), hexadecane (bp of 280°C.), octadecane (bp of 308°C.) and nonadecane (bp of 320°C.); glycol ethers exemplified by diethylene glycol ethyl ether (bp of 202°C.), diethylene glycol butyl ether (bp of 230°C.), triethylene glycol methyl ether (bp of 242°C.), triethylene glycol ethyl ether (bp of 254°C.), triethylene glycol butyl ether (bp of 283°C.), ethylene glycol phenyl ether (bp of 245°C.), propylene glycol phenyl ether (bp of 243°C.) and aromatic based glycol ethers (bp of 245°C.); esters exemplified by diethylene glycol butyl ether acetate (bp of at least 235°C.), pine oil (bp of at least 212°C.) and mineral seal oil (bp of at least 278°C.); alcohols exemplified by tridecyl alcohol (bp of 252°C.) and ester alcohols including trimethyl pentane diol isobutyrate (bp of at least 244°C.); ketones exemplified by isophorone (bp of at least 215°C.), kerosenes, naphthas and petrolatums; carboxylic acids having at least six carbon atoms exemplified by nonanoic acid (bp of 268°C.), caproic acid (also known as hexanoic acid (bp of 202°C.), caprylic acid (also known as octanoic acid (bp of 237°C.), oleic acid, linoleic acid, linolenic acid and N-coco-beta-aminobutyric acid and amines having at least nine carbon atoms exemplified by dodecylamine (bp of 248°C.), hexadecylamine (bp of 330°C.), octadecylamine, dimethyldodecylamine, dicocoamine, methyldicocoamine, dimethyl cocoamine, dimethyltetradecylamine, dimethylhexadecylamine, dimethyloctadecylamine, dimethyl tallow amine, dimethylsoyaamine, dimethyl nonylamine, di(hydrogenated-tallow)amine and methyldi(hydrogenated-tallow)amine. Particularly useful solvents from the standpoint of their physical and chemical properties are the branch-chain isoparaffinic solvents sold by the Exxon Chemical Company under the tradenames Exxsol® D 110, Isopar® M or Isopar® V. It is preferred that the solvent or plasticizer of component (D) have a boiling point of at least 210°C., and it is especially preferred that the solvent or plasticiser of (D) have a boiling point of at least 225°C. It is preferred that component (D) is miscible in components (A) and (B). Miscible as used herein denotes that Component (D) has the ability to dissolve uniformly in the mixture of (A)+(B).

The amount of component (D) to be used is dependent on the type of solvent or plasticizer selected. If a solvent or plasticizer having a boiling point near 200°C. is selected, a greater amount of solvent or plasticizer is required. The amount of component (D) in the compositions of this invention is from 2 to 40 parts by weight and, more preferably, from 5 to 30 parts by weight per 100 parts by weight of components (A)+(B).

The mixture of step (I) can further comprise a rare earth metal salt of a fatty acid. Examples of rare earth metals suitable for forming the salt include cerium, lanthanum, praseodymium, with cerium being preferred. The fatty acid generally contains 6 to 18 carbon atoms, most preferable are 8 carbon atoms. The preferred rare earth metal salt is cerium octoate. The rare earth metal salt is used in the compositions of this invention to provide the composition with an amount of rare earth metal within the range of from 1 to 1000 parts by weight, and from 10 to 250 parts by weight, per one million parts by weight of components (A)+(B). Typically, the rare earth metal salt, if used, is in the form of a 30% solvent solution, 6% of which is composed of the active rare earth metal. Solvents suitable for the rare earth metal solution have a boiling point of less than 200°C.; namely, hexane, heptane, toluene, xylene, naphtha, mineral spirits or ketones.

The reaction product of step (I) is made by reacting a mixture of components (A), (B), (C) and (D). Reacting for the purposes of this invention denotes simply mixing components (A), (B), (C) and (D) and any optional components at room temperature (25°C.) or heating a mixture of components (A)-(D) and any optional components at temperatures above room temperature. Preferably, a mixture of components (A)-(D) and any optional components are heated at a temperature above 100°C. A preferred embodiment of the reaction process is to pre-neutralize or otherwise pacify catalytic impurities which are often introduced with the raw materials of the adhesive reaction product. The reaction product is also formed by reacting a mixture of components (A), (B) and (C), and then adding component (D), and then optionally heating the resulting product to form a reaction product. The mixing of these components is enhanced, if desired, by the use of one or more solvents having a boiling point of less than 200°C. in the mixture of step (I); namely, benzene, toluene, xylene, naphtha, mineral spirits, cyclic polysiloxanes or alcohols; namely, methanol, ethanol, isopropanol, butanol, or n-propanol. The amount of solvent having a boiling point of less than 200°C., if used, ranges from 60 to 200 parts by weight per 100 parts by weight of components (A)+(B). The mixture of (A)-(D) is heated for 4 hours at temperatures of 100 to 180°C.; however, the time and temperature are dependent on the selection and concentration of the reaction components. The reaction is complete when the viscosity of the reaction product remains constant or slightly decreases after achieving a maximum value. The reacting of the mixture of (A)-(D) results in the formation of a reaction product.

When a solvent having a boiling point of less than 200°C. is used, it is necessary to remove this solvent after the formation of the reaction product. Methods of removing volatile components are well known in the art and need no extensive delineation herein. Any method of removing volatile components can be used, such methods exemplified by molecular stills, rotoevaporators and wipe film evaporators, with the preferred method being rotoevaporators.

It is preferred that the reaction product of step (I) have a solids content of at least 60% and a viscosity of 200,000 mPa · s, more preferably, has a solids content of at least 75% and a viscosity of 150,000 mPa · s; and it is highly preferred that the reaction product of step (I) has a solids content of at least 80% and a viscosity of up to 100,000 mPa · s.

In step (II), component (E) an organic peroxide or azo compound is added to the reaction product of step (I). Examples of preferred organic peroxides which are suitable as component (E) include diacyl peroxides; namely, benzoyl peroxide or dichlorobenzoyl peroxide. Benzoyl peroxide is a particularly effective organic peroxide.

Examples of azo compounds suitable as component (E) include azobenzene, azobenzene-p-sulfonic acid, 2,4-dimethyl-4-methoxyvaleronitrile, azobisdimethylvaleronitrile, azobisisobutyronitrile or azodine, with azobisisobutyronitrile being preferred. Component (E) when added to the product of step (I) is added as a solution, for example, in an appropriate solvent having a boiling point of less than 200°C.; namely, benzene, toluene, xylene, naphtha, chlorocarbons, ketones or mineral spirits.

The amount of Component (E) in the compositions of this invention is from 0.1 to 5 parts by weight and, more preferably, from 1.5 to 3.5 parts by weight per 100 parts by weight of components (A)+(B).

During or after the formation of the silicone pressure sensitive adhesive composition, small amounts of additional ingredients may be added to the composition so long as they do not materially affect the pressure sensitive adhesive composition. These additional ingredients are exemplified by, but not limited to, antioxidants, pigments, stabilizers and fillers. It is apparent that a blend of two or more reaction products, each having different amounts of components (A), (B), (C) and/or (D), is formed in Step (I), and then this blend is catalyzed according to Step (II).

Our invention further provides articles of manufacture prepared by (I) applying a silicone pressure sensitive adhesive composition to at least one surface of a substrate, wherein the silicone pressure sensitive adhesive composition is as described above including preferred embodiments thereof and (II) heating the silicone pressure sensitive adhesive composition and the substrate to cure the composition. The method can further comprise (III) contacting a solid support with the substrate having the adhesive composition cured thereon after step (II) whereby the solid support and the substrate are adhered together.

The silicone pressure sensitive adhesive compositions of this invention are useful to adhere a substrate to a solid support, whether flexible or rigid. These compositions may be applied to a surface by any suitable means; namely, rolling, spreading or spraying and then cured as described above.

The surface of the solid support and the substrate to which the solid support is adhered may be any known solid material such as metals; namely, aluminum, silver, copper, iron and their alloys; porous materials such as paper, wood,

leather and fabrics; organic polymeric materials such as polyolefins including polyethylene and polypropylene; fluoro-carbon polymers; namely, polytetrafluoroethylene and polyvinylfluoride; silicone elastomers and resins, polystyrene, polyamides; namely, nylon, polyimides, polyesters and acrylic polymers; painted surfaces, siliceous materials; namely, concrete, bricks, cinderblocks and glass such as glass cloth. Porous materials like glass cloth are often impregnated with a substance that will prevent the migration of the silicone pressure sensitive adhesive from one surface to another surface of the support. In this regard, it is also well known to chemically treat, physically treat (for example, etching) or primecoat (adding a curable polysiloxane) the surface of a substrate prior to addition of silicone pressure sensitive adhesive compositions so as to enhance adhesion to said surface. Our invention is particularly suited to applications wherein good adhesion to a low energy surface (e.g., polyethylene or Teflon[®]) is desired.

The amount of silicone pressure sensitive adhesive composition applied to surfaces is sufficient to render the surface tacky to the touch after the removal of any solvent having a boiling point of less than 200°C. After applying it to the surface, the adhesive is cured by air drying or heating at temperatures of up to 300°C.

Solid supports bearing the cured compositions of our invention are readily adhered to any solid substrate because the silicone pressure sensitive adhesive compositions of this invention have high tack and good adhesive strength.

Useful articles which are prepared with the silicone pressure sensitive adhesive compositions of this invention include pressure sensitive tapes, labels, emblems and other decorative or informational signs. In particular, our silicone pressure sensitive adhesive compositions are useful in tapes; namely, splicing tape in label and paper stock manufacture and converting. An especially useful article is one comprising a flexible or rigid support that withstands extreme temperatures, hot and/or cold, and carrying on at least one surface thereof the silicone pressure sensitive adhesive composition of our invention. Such an article makes full use of the stability at high temperatures and the flexibility at low temperatures that the silicone pressure sensitive adhesive compositions of this invention possess.

All parts and percentages are on a weight basis and all measurements were obtained at 25°C. unless otherwise indicated. The molecular weight properties of the polydimethylsiloxane polymers below were determined by Gas Phase Chromatography (GPC) in a toluene solvent, and using a polydimethylsiloxane standard.

The apparatus and testing procedures used for the results shown herein are as follows:

Adhesion was measured by applying a 6 x 1 inch strip of a Kapton[®] or Mylar[®]-backed adhesive to a clean 2 x 6 inch stainless steel panel using two passes of a 4.5 lb. rubber-coated roller. The force required to remove the tape from the panel was measured with a Keil Tester at an peel angle of 180° at a rate of 12 inches per minute. The values recorded are the average of multiple readings taken during the course of one pull per sample. The Keil Tester is described in TAPPI, vol. 43, No. 8., pages 164A and 165A (August 1960). The readings are reported in units of ounces per inch (oz/in), as specified in said article.

Tack was measured on at least five 2.54 cm squares of the Kapton[®] or Mylar[®]-backed adhesive using a POLYKEN[®] probe tack tester, available from Testing Machines, Inc., Amityville, NY. The tack tester has a 0.5 cm diameter stainless steel probe. The test procedure used a 20 gram weight, a dwell time of 1.0 second and a pull speed of 0.5 cm per second. The results reported represent the average of at least five readings, expressed in g/cm².

Non-volatile content, i.e. percent solids, of an adhesive material was determined by heating a two gram sample of the material at 150°C. for one hour and expressing the weight of the residue as a percentage of the original sample weight.

The non-volatile content of the MQ resins was determined by mixing 1.5 g of resin solution with 0.75 g of a polydimethylsiloxane fluid having a viscosity of 100 centistokes (cS) (100 mm²/s), followed by devolatilization at 150°C. for 2 hours.

The resins in the examples were analyzed using ²⁹Si NMR to determine the molar ratios of the (CH₃)₃SiO_{1/2} units (M) to SiO_{4/2} units (Q) in each resin and to determine the hydroxyl content of each resin.

Viscosities were measured in centipoise (cP) (1 cP = 1 millipascal-second (mPa · s)) at room temperature (25° ± 2°C.) using a Brookfield rotating disc viscometer fitted with an LV-4 spindle.

The following materials were employed in preparing the compositions in the examples:

POLYMER A was a hydroxyl-endblocked polydimethylsiloxane fluid having a viscosity of 15,000 mPa · s, a number average molecular weight (Mn) of 38,200 and a weight average molecular weight (Mw) of 68,470.

POLYMER B was a hydroxyl-endblocked polydimethylsiloxane gum copolymer containing 4 mole% MeViSiO repeat units and having a plasticity of 0.15 mm as measured by ASTM D926-27.

POLYMER C was a hydroxyl-endblocked polydimethylsiloxane gum, having a plasticity of 0.147 mm as measured by ASTM D926-27.

RESIN A was a benzene-soluble, siloxane resin consisting of (CH₃)₃SiO_{1/2} (M) units and SiO_{4/2} (Q) units and having an M:Q molar ratio of 0.78:1.0, a hydroxyl content of 2.9 wt%, and the following molecular weight characteristics as determined by GPC in Chloroform, using fractionated MQ resin standards and an IR detector, an Mn of 4,300, an Mw of 14,600 and an Mw/Mn of 3.395.

RESIN B was a benzene-soluble, siloxane resin consisting of (CH₃)₃SiO_{1/2} (M) units and SiO_{4/2} (Q) units and hav-

ing a non-volatile content of 63.5%, and a hydroxyl content of < 1.0%.

THERMAL STABILITY ADDITIVE was Ten-Cem[®] (a dispersion of a neodecanoate salt of a rare earth metal in mineral spirits having 6% active metals in the mineral spirits from Mooney Chemicals, Inc., Cleveland, Ohio).

5 PEROXIDES:

Perkadox[®] PD-50S-ps-a - a suspension of 50 wt% 2,4-dichlorobenzoyl peroxide in a proprietary polysiloxane fluid supplied by Akzo Chemical.

Benzoyl peroxide, in granular form, was 98% pure supplied by Aldrich Chemical Company.

10

EXAMPLE 1

First 150.1 g of Resin A, 73.6 g of Polymer A, 76.3 g of toluene, 20 g Exxsol[®] D-110 Solvent (a C₉-C₁₆ branched chain aliphatic hydrocarbon petroleum distillate having a boiling point ranging from 237 to 277°C. from Exxon Chemical Company, a Division of Exxon Corporation, Houston, Texas), 4.6 g of triethylamine, and 0.06 g of a thermal stability additive, were combined in a 500ml 3-neck flask equipped with stirrer, thermometer, Dean Stark trap and condenser. The contents were mixed and heated to reflux temperature (125°C.) where it was maintained for 4 hours. Water was removed continuously during the reflux step. Half way through the stripping process, 20 g of Exxsol[®] D-110 was added to the mixture which was conducted at elevated temperature and at atmospheric pressure. The stripping process was resumed until the pot temperature reached 205°C. The reaction product was then allowed to cool prior to recovery and storage for evaluation. This product had a measured viscosity of 35,500 mPa · s at 86% solids.

A portion of the product was catalyzed by adding Perkadox[®] PD-50S-ps-a to the reaction product at a level of 2 wt% peroxide solids based on the solids, and cast onto 25.4 µm polyimide (Kapton[®]) in an amount sufficient to attain a 25.4 µm dry film on the substrate. The polyimide supported film was cured for 5 minutes at 204°C. The same catalyzed mixture was also cast onto a sheet of 50.8 µm Mylar[®] A and cured for 5 minutes at 178°C. The samples were then measured for probe tack and 180 degree peel adhesion as described above. The results are shown in Table 1.

In a separate evaluation, a second portion of the adhesive was catalyzed with Perkadox[®] PD-50S-ps-a at the same level described above and cast onto sheets of 25.4 µm polyester (Mylar[®] A) and 0.00254 polyimide (Kapton[®]). Each sheet was then cured by a different set of thermal conditions, followed by evaluation of 180 degree Peel Adhesion and Probe Tack as described above. The results are recorded in Table 2.

30

COMPARATIVE EXAMPLE 1

Next 150.1 g of Resin A, 73.6 g of Polymer A, 76.3 g of toluene, 4.6 g of triethylamine and 0.06 g of a thermal stability additive, were combined in a 500 ml 3-neck flask equipped with stirrer, thermometer, Dean Stark trap and condenser. After refluxing for 4 hours, with continuous removal of water from the process, the mixture was stripped to 84% solids. The resultant adhesive product was then cooled, recovered and stored for evaluation.

A portion of the adhesive product was catalyzed with Perkadox[®] PD-50S-ps-a at a level of 2 wt% peroxide solids based on solids and cast onto 25.4 µm polyimide (Kapton[®]) in an amount sufficient to attain a 25.4 µm dry film on the substrate. The polyimide supported film was cured for 2 minutes at 70°C. followed by an additional 2 minutes at 204°C. The same catalyzed mixture was also cast onto a sheet of 25.4 µm Mylar[®] A, and cured for 2 minutes at 70°C. followed by an additional 2 minutes at 178°C. The probe tack and 180 degree Peel Adhesion were then measured as above. The results are recorded in Table 3.

40

45 COMPARATIVE EXAMPLE 2

Then 150.1 g of Resin A, 73.6 g of Polymer A, 76.3 g of toluene, 4.6 g of triethylamine and 0.06 g of a thermal stability additive, were combined in a 500 ml 3-neck flask equipped with stirrer, thermometer, Dean Stark trap and condenser. After refluxing for 4 hours, with continuous removal of water from the process, the product was stripped to remove the aromatic solvents contained in the crude mixture. Then, 20 g of heptane solvent was then added to the stripped product, resulting in a non-volatile content of 90%. The resultant product was cooled, recovered and stored for evaluation.

50

A portion of the adhesive product was catalyzed with Perkadox[®] PD-50S-ps-a at a level of 2 wt% peroxide solids based on the solids, and cast onto a sheet of 25.4 µm Mylar[®] A, in an amount sufficient to attain a 25.4 µm dry film thickness on the substrate. The polyester supported film was cured for 2 minutes at 70°C. followed by an additional 2 minutes at 178°C. Prob Tack and 180 degree Peel Adhesion were then measured as above. Results are recorded below.

55

SUBSTRATE	180° PEEL ADHESION	PROBE TACK
25.4 μ m Mylar® A	52 oz/in	998 +/- 38 g/cm ²

Using the same catalyzed mixture, a second polyester sheet was coated and cured for 5 minutes at 178°C. Probe Tack and 180 degree Peel Adhesion were then measured as above. Results are recorded below.

SUBSTRATE	180° PEEL ADHESION	PROBE TACK
25.4 μ m Mylar® A	49 oz/in	1,098 +/- 82 g/cm ²

EXAMPLE 2

Thereafter, 150.1 g of Resin A, 73.6 g of Polymer A, 76.3 g of toluene, 4.6 g of Triethylamine and 0.06 g of a thermal stability additive, were combined in a 500 ml 3-neck flask equipped with stirrer, thermometer, Dean Stark trap and condenser. The contents were mixed well and heated to reflux temperature where it was maintained for 4 hours. Water was removed continuously during the reflux step. Next 9.5 g Exxsol® D-110 was added to the product and the resulting reaction product (adhesive) was then stripped at atmospheric pressure to 91% solids, cooled, recovered and stored for evaluation.

A portion of the adhesive product was catalyzed with Perkadox® PD-50S-ps-a at a level of 2 wt% peroxide solids based on the solids and then cast onto 25.4 μ m polyimide (Kapton®) using a Bird Bar to attain a 25.4 μ m dry film on the substrate. The polyimide supported film was cured for 2 minutes at 70°C. followed by an additional 2 minutes at 204°C. The same catalyzed mixture was also cast onto a sheet of 25.4 μ m Mylar® A and cured for 2 minutes at 70°C. followed by an additional 2 minutes at 178°C. Probe Tack and 180 degree Peel Adhesion were then measured as above. Results are recorded in Table 4.

EXAMPLE 3

Then 150.1 g of Resin A, 73.6 g of Polymer A, 76.3 g of toluene, 4.6 g of triethylamine and 0.06 g of a thermal stability additive, were combined in a 500 ml 3-neck flask equipped with stirrer, thermometer, Dean Stark trap and condenser. The contents were well mixed and heated to reflux temperature where it was maintained for 4 hours. Water was removed continuously during the reflux step. Thereafter, 45 g Exxsol® D-110 was added to the reaction product (adhesive), which was then stripped at atmospheric pressure to 76% solids, cooled, recovered and stored for evaluation at a future date.

A portion of the adhesive product was catalyzed with Perkadox® PD-50S-ps-a at a level of 2 wt% peroxide solids based on the solids and cast onto 25.4 μ m polyimide (Kapton®) using a Bird Bar to attain a 25.4 μ m dry film on the substrate. The polyimide supported film was cured for 2 minutes at 70°C. followed by an additional 2 minutes at 204°C. The same catalyzed mixture was also cast onto a sheet of 25.4 μ m Mylar® A and cured for 2 minutes at 70°C. followed by an additional 2 minutes at 178°C. The Probe Tack and 180 degree Peel Adhesion were then measured as above. Results are recorded in Table 5.

EXAMPLE 4

Then 150.1 g of Resin A, 73.6 g of Polymer A, 76.3 g of toluene, 4.6 g of triethylamine and 0.06 g of a thermal stability additive, were combined in a 500 ml 3-neck flask equipped with stirrer, thermometer, Dean Stark trap and condenser. The contents were well mixed and heated to reflux temperature where it was maintained for 4 hours. Water was removed continuously during the reflux step. Thereafter, 20 g Isopar® M (a C₁₃-C₁₄ branched chain aliphatic hydrocarbon petroleum distillate having a boiling point ranging from 207°C. to 254°C. marketed by Exxon Chemical Company, a Division of Exxon Corporation, Houston, Texas) was added to the mixture, which was then stripped at atmospheric pressure to 86% solids, cooled, recovered and stored for evaluation.

A portion of the adhesive was catalyzed with Perkadox® PD-50S-ps-a at a level of 2 wt% peroxide solids based on the solids and cast onto 25.4 μ m polyimide (Kapton®) using a Bird Bar to attain a 25.4 μ m dry film on the substrate. The polyimide supported film was cured for 2 minutes at 70°C. followed by an additional 2 minutes at 204°C. The same

mixture was also cast onto a sheet of 25.4 μm polyester (Mylar[®] A), and cured for 2 minutes at 70°C. followed by an additional 2 minutes at 178°C. The Probe Tack and 180 degree Peel Adhesion were then measured as above. The results are recorded in Table 6.

5 EXAMPLE 5

Then 150.1 g of Resin A, 73.6 g of Polymer A, 76.3 g of toluene, 4.6 g of triethylamine and 0.06 g of a thermal stability additive, were combined in a 500 ml 3-neck flask equipped with stirrer, thermometer, Dean Stark trap and condenser. The contents were well mixed and heated to reflux temperature where it was maintained for 4 hours. Water was removed continuously during the reflux step. Thereafter 20 g Isopar[®] V (a C₁₄-C₁₈ branched chain aliphatic hydrocarbon petroleum distillate having a boiling point ranging from 254°C., to 329°C., marketed by Exxon Chemical Company, a Division of Exxon Corporation, Houston, Texas) was added to the reaction product (adhesive), which was then stripped to 86% solids, cooled, recovered and stored for evaluation.

A portion of the adhesive was catalyzed with Perkadox[®] PD-50S-ps-a at a level of 2 wt% peroxide solids based on the solids, and cast onto 25.4 μm polyimide (Kapton[®]) using a Bird Bar to attain a 25.4 μm dry film on the substrate. The polyimide supported film was cured for 2 minutes at 70°C. followed by an additional 2 minutes at 204°C. The same catalyzed mixture was also cast onto a sheet of 25.4 μm Mylar[®] A and cured for 2 minutes at 70°C. followed by an additional 2 minutes at 178°C. The Probe Tack and 180 degree Peel Adhesion were then measured as described above. The results are recorded in Table 7.

20 EXAMPLE 6

Then 133.7 g of Resin A, 85.5 g of polymer A, 80.9 g of toluene, 0.06 g of a thermal stability additive and 4.6g triethylamine were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. The mixture was heated to reflux, and maintained at reflux, for 4 hours. Water was continuously removed during the reflux step. Thereafter, 20 grams of Exxsol[®] D-110 Solvent were added to the reaction product which was then reheated and stripped at atmospheric pressure to the desired nonvolatiles content in the range of 85% solids. The viscosity of the resultant reaction product was 32,250 mPa · s at 83.9% solids.

30 EXAMPLE 7

Then 174.0 g of Resin A, 56.4 g of polymer A, 69.6 g of toluene, 0.06 g of a thermal stability additive and 4.6g of triethylamine were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. The mixture was heated to reflux, and maintained at reflux, for 4 hours. Water was continuously removed during the reflux step. Thereafter, 20 g of Exxsol[®] D-110 were then added to the reaction product which was then reheated and stripped at atmospheric pressure to the desired nonvolatiles content in the range of 85% solids. The viscosity of the resultant reaction product was 12,200 mPa · s at 84.8% solids.

40 EXAMPLE 8

A pressure sensitive adhesive blend was prepared by combining 3 parts of the product of Example 5, per 1 part of the product of Example 6, then mixing until a uniform dispersion was obtained. The mixture was catalyzed, using a 10% solution of benzoyl peroxide in methyl ethyl ketone at a benzoyl peroxide level of 2% based on solids. The catalyzed solution was then cast onto 25.4 μm Polyester film (Mylar[®] A) in an amount sufficient to attain a 25.4 μm dried film. The cast film was devolatilized for 2 minutes at 70°C. and then cured for 2 additional minutes at 178°C. The resultant film laminate was then cut into 2.54 cm wide strips and evaluated for adhesive performance. The Probe Tack and 180 degree Peel Adhesion were then measured as above. The Peel Adhesion of this composition was 52 oz/in and the Probe Tack was 1,368 g/cm².

50 EXAMPLE 9

Then 133.7 g of Resin A, 78.1 g of polymer A, 7.4 g of polymer B, 80.9 g of toluene, 0.06 g of a thermal stability additive and 4.6 g triethylamine, were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. The mixture was heated to reflux and maintained at reflux for 4 hours. Water was continuously removed during the reflux step. Thereafter, 20 g of Exxsol[®] D-110 were added to the reaction product which was then reheated and stripped at atmospheric pressure to the desired nonvolatiles content in the range of 85% solids. The viscosity of the resultant reaction product was 100,000 mPa · s at 86% solids.

EXAMPLE 10

Then 174.0 g of Resin A, 51.5 g of polymer A, 4.9 g of polymer B, 69.6 g of toluene, 0.06g of a thermal stability additive and 4.6 g triethylamine, were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. The mixture was heated to reflux, and maintained at reflux, for 4 hours. Water was continuously removed during the reflux step. Thereafter, 20 g of Exxsol® D-110 were then added to the reaction product, which was then reheated and stripped at atmospheric pressure to the desired nonvolatiles content in the range of 85% solids. The viscosity of the resultant reaction product was 32,250 mPa · s at 86.4% solids.

EXAMPLE 11

A pressure sensitive adhesive blend was prepared by combining 3 parts of the product described in Example 8, per 1 part of the product described in Example 9, then mixing until a uniform dispersion was obtained. The mixture was catalyzed, using a 10% solution of benzoyl peroxide in methyl ethyl ketone, at a benzoyl peroxide level of 2% based on solids. The catalyzed blend was then cast onto 25.4 µm Polyester film (Mylar® A) in an amount sufficient to attain a 25.4 µm, dried film. The cast film was devolatilized for 2 minutes at 70°C. and then cured for 2 additional minutes at 178°C. The resultant sheet supporting the film was then cut into 2.54 cm wide strips and evaluated for performance. The Probe Tack and 180 degree Peel Adhesion were then measured as above. The Peel Adhesion of this composition was 56 oz/in and the Probe Tack was 1,326 g/cm².

EXAMPLE 12

Next 150.1 g of Resin A, 73.6 g of polymer A, 58.3 g of toluene, 18.0 g of tetradecane, 0.06 g of a thermal stability additive and 4.6 g triethylamine were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. The mixture was heated to reflux, and maintained at reflux, for 4 hours. Water was continuously removed during the reflux step. The reaction product (adhesive) was then stripped at atmospheric pressure to 86% solids.

A portion of the adhesive was catalyzed with Perkadox® PD-50S-ps-a at a level of 2 wt% peroxide solids based on the solids. The catalyzed mixture was cast onto 25.4 µm polyester film (Mylar® A), devolatilized for 2 minutes at 70°C. and finally cured for an additional 2 minutes at 178°C. The thickness of the film was 48.26 µm. The Probe Tack and 180 degree Peel Adhesion were then measured as above. The Peel Adhesion of this silicone pressure sensitive adhesive composition was 59 oz/in and the Probe Tack was 1,304 g/cm².

EXAMPLE 13

Next 150.1 g of Resin A, 73.6 g of polymer A, 58.3 g of toluene, 18.0 g of hexadecane, 0.06 g of a thermal stability additive and 4.6 g triethylamine were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. The mixture was heated to reflux, and maintained at reflux, for 4 hours. Water was continuously removed during the reflux step. The reaction product (adhesive) was then stripped at atmospheric pressure to 85.5% solids.

A portion of the adhesive was catalyzed with Perkadox® PD-50S-ps-a at a level of 2 wt% peroxide solids based on solids. The catalyzed mixture was cast onto 25.4 µm polyester film (Mylar® A), devolatilized for 2 minutes at 70°C. and finally cured for an additional 2 minutes at 178°C. The thickness of the film was 48.26 µm. The Probe Tack and 180 degree Peel Adhesion were then measured as above. The Peel Adhesion of this silicone pressure sensitive adhesive composition was 70 oz/in and the Probe Tack was 1,380 g/cm².

EXAMPLE 14

Next 150.1 g of Resin A, 73.6 g of polymer A, 58.3 g of toluene, 18.0 g of octadecane, 0.06 g of a thermal stability additive and 4.6 g triethylamine were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. The mixture was heated to reflux, and maintained at reflux, for 4 hours. Water was continuously removed during the reflux step. The reaction product (adhesive) was then stripped at atmospheric pressure to 86% solids.

A portion of the adhesive was catalyzed with Perkadox® PD-50S-ps-a at a level of 2 wt% peroxide solids based on the solids. The catalyzed mixture was cast onto 25.4 µm polyester film (Mylar® A), devolatilized for 2 minutes at 70°C. and finally cured for an additional 2 minutes at 178°C. The thickness of the film was 48.26 µm. The Probe Tack and 180 degree Peel Adhesion were then measured as above. The Peel Adhesion of this composition was 72 oz/in and the Probe Tack was 1,351 g/cm².

EXAMPLE 15

Several samples were prepared by mixing 150.1 g of Resin A, 73.6 g of polymer A, an amount of toluene, an amount of a solvent having a high boiling point (denoted HBS (High Boiling Solvent) in Table 8), 0.06 g of a thermal stability additive and an amount of catalyst were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. Each mixture was heated to reflux, and maintained at reflux, for 4 hours. Water was continuously removed during the reflux step. Each reaction product was then stripped at atmospheric pressure, and the solids content and viscosity of each sample is recorded in Table 9. The amount of toluene, the amount and type of solvent, and the amount and type of catalyst are delineated in Table 8 below. TEA denotes triethylamine, Dowanol[®]ODPM is dipropylene glycol methyl ether having a boiling point of 188°C. from Dow Chemical Company, Dowanol[®]TPM is tripropylene glycol methyl ether having a boiling point of 242°C. also from Dow Chemical Company and Dowanol[®]PPh is propylene glycol phenyl ether having a boiling point of 242°C. also from Dow Chemical Company. Dowanol[®]TPM was not entirely miscible in the resin-polymer mixture.

A portion of each adhesive was catalyzed with Perkadox[®] PD-50S-ps-a at a level of 2 wt% peroxide solids based on the solids. Each catalyzed mixture was cast onto 25.4 μ m polyester film (Mylar[®] A), devolatilized for 2 minutes at 70°C. and finally cured for an additional 2 minutes at 178°C. The thickness of the film was 0.00483mm. The Probe Tack and 180 degree Peel Adhesion were then measured as above and the results are shown in Table 9. The Peel Adhesion was measured in oz/in and the Probe Tack was measured in g/cm².

EXAMPLE 16

Then 80.3 g of Resin A, 19.7 g of Resin B, 55.7 g of polymer C, 144.2 g of xylene, 3.0 g of triethylamine, 5.0 g nonanoic acid and 0.04 g of a thermal stability additive were combined and thoroughly blended in a three-necked flask equipped with a stirrer, thermometer, condenser and Dean Stark Trap. The mixture was heated to reflux, and maintained at reflux, for 4 hours. Water was continuously removed during the reflux step. The reaction product (adhesive) was then stripped at atmospheric pressure, followed by addition of an additional 7.0 g of nonanoic acid. The non-volatile content for the resultant composition was 54.6% solids.

A portion of the adhesive was catalyzed with a 10% solution of benzoyl peroxide in toluene, at a level of 2 wt% peroxide solids based on the solids. The catalyzed mixture was cast onto a primed 25.4 μ m Kapton[®] film, devolatilized for 2 minutes at 70°C. and finally cured for an additional 2 minutes at 204°C. The thickness of the film was 25.4 μ m. The Probe Tack and 180 degree Peel Adhesion were measured as above. The Peel Adhesion of this composition was 20 oz/in, and the Probe Tack was 1,095 g/cm².

Table 1

SUBSTRATE	180° PEEL ADHESION*	PROBE TACK
25.4 μ m MYLAR [®] A	51 oz/in	1,286 +/- 47 g/cm ²
25.4 μ m KAPTON [®]	33 oz/in	967 +/- 59 g/cm ²

* reported in oz/in as specified in Tappi 43 (8), 164-165, 1960

Table 2

SHEET TYPE	CURE CONDITIONS	180° PEEL ADHESION*	PROBE TACK
25.4 μ m KAPTON [®]	2 min. @ 70°C. then 2 min. @ 204°C.	36 oz/in	981 +/- 25 g/cm ²
25.4 μ m KAPTON [®]	2 min. @ 204°C.	36 oz/in	988 +/- 31 g/cm ²
25.4 μ m MYLAR [®] A	2 min. @ 70°C. then 2 min. @ 178°C.	56 oz/in	1,334 +/- 62 g/cm ²
25.4 μ m MYLAR [®] A	2 min. @ 178°C.	55 oz/in	1,262 +/- 88 g/cm ²

* reported in oz/in as specified in Tappi 43 (8), 164-165, 1960

Table 3

SUBSTRATE	180° PEEL ADHESION*	PROBE TACK
25.4 μ m MYLAR® A	51 oz/in	1,101 +/- 43 g/cm ²
25.4 μ m KAPTON®	28 oz/in	925 +/- 29 g/cm ²

* reported in oz/in as specified in Tappi 43 (8), 164-165, 1960

Table 4

SUBSTRATE	180° PEEL ADHESION*	PROBE TACK
25.4 μ m MYLAR® A	55 oz/in	1,338 g/cm ²
25.4 μ m KAPTON®	32 oz/in	1,058 g/cm ²

* reported in oz/in as specified in Tappi 43 (8), 164-165, 1960

Table 5

SUBSTRATE	180° PEEL ADHESION*	PROBE TACK
25.4 μ m MYLAR® A	71 oz/in	1,442 g/cm ²
25.4 μ m KAPTON®	42 oz/in	1,097 g/cm ²

* reported in oz/in as specified in Tappi 43 (8), 164-165, 1960

Table 6

SUBSTRATE	180° PEEL ADHESION*	PROBE TACK
25.4 μ m MYLAR® A	52 oz/in	1,111 g/cm ²
25.4 μ m KAPTON®	29 oz/in	894 g/cm ²

* reported in oz/in as specified in Tappi 43 (8), 164-165, 1960

Table 7

SUBSTRATE	180° PEEL ADHESION*	PROBE TACK
25.4 μ m MYLAR® A	58 oz/in	1,253 g/cm ²
25.4 μ m KAPTON®	32 oz/in	1,023 g/cm ²

* reported in oz/in as specified in Tappi 43 (8), 164-165, 1960

Tabl 8

Sample	Toluene (grams)	HBS Type	HBS (grams)	Catalyst Type	Catalyst (grams)
1	58.3	Dowanol® DPM	18	Pyridine	3.6
2	58.3	Dowanol® TPM	18	Pyridine	3.6
3	40.3	Dowanol® PPh	36	Pyridine	3.6
4	22.3	Isopar® M	54	TEA**	4.6
5	40.3	Isopar® M	36	TEA	4.6
6	76.3	Isopar® M	0	TEA	4.6
7	58.3	Octadecane	18	TEA	4.6
8	58.3	Hexadecane	18	TEA	4.6
9	58.3	Tetradecane	18	TEA	4.6
10	22.3	Decane	54	TEA	4.6
11	22.3	Undecane	54	TEA	4.6
12	22.3	Dodecane	54	TEA	4.6

**TEA = triethylamine

Table 9

Sample	Viscosity (mPa · s)	% Solids	Peel Adhesion* (oz/in)	Probe Tack (g/cm ²)
1	470,000	88	48	864
2	1,190,000	89	44	601
3	53,000	79	48	1,304
4	4,200	73	58	1,190
5	11,500	81	63	1,034
6	43,500	89	60	1,001
7	N/A	86	>70	1,351
8	N/A	86	70	1,380
9	N/A	86	59	1,304
10	16,500	86	46	1,014
11	5,500	79	44	956
12	2,900	74	48	1,097

* reported in oz/in as specified in Tappi 43 (8), 164-165, 1960

Claims

1. A silicone pressure sensitive adhesive composition obtainable by a method comprising the steps of (I) reacting a mixture comprising

(A)(i) at least one hydroxyl-terminated polydiorganosiloxane having a viscosity of from 100 to 100,000,000 mm²/s at 25°C. or (ii) a mixture of (a) a hydroxyl-terminated polydiorganosiloxane and (b) a polydiorganosiloxane selected from (i) polydiorganosiloxanes terminated with monovalent hydrocarbon radicals free of

aliphatic unsaturation or (ii) alkenyl-terminated polydiorganosiloxanes wherein said mixture has a viscosity of from 100 to 100,000,000 mm²/s at 25°C.;

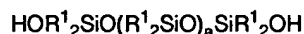
(B) at least one soluble silicone resin essentially consisting of at least one R₃SiO_{1/2} unit and at least one SiO_{4/2} unit, wherein R is independently selected from a monovalent hydrocarbon or halohydrocarbon radical free of aliphatic unsaturation and having from 1 to 20 carbon atoms, an alkenyl radical or a hydroxyl radical wherein the molar ratio of R₃SiO_{1/2} units to SiO_{4/2} units is from 0.5:1 to 1.2:1;

(C) at least one silanol condensation catalyst selected liquid catalysts having a boiling point of less than 200°C. or catalysts which are solid at room temperature; and

(D) at least one solvent or plasticizer having a boiling point of at least 200°C. to form a reaction product; and

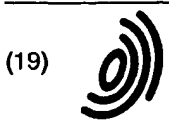
(II) adding (E) an organic peroxide or azo compound to the reaction product of (I).

2. The composition of claim 1 wherein the hydroxyl-terminated polydiorganosiloxane is a polydiorganosiloxane having the general formula



wherein each R¹ is independently selected from a monovalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms or an alkenyl radical and "a" has a value such that the viscosity of said polydiorganosiloxane ranges from 1,000 to 500,000 mm²/s when measured at 25°C.

3. The composition of claim 1 wherein R is independently selected from methyl, phenyl, vinyl or hydroxyl, the molar ratio of R₃SiO_{1/2} units to SiO_{4/2} units is from 0.6:1 to 1:1 and (B) has a number average molecular weight of 3,000 to 7,500.
4. The composition of claim 1 wherein (C) is selected from alkali metal hydroxides, alkali metal alkoxides, alkali metal carbonates, alkali metal silanates, amines, carboxylic acid salts of amines, quaternary ammonium salts, carboxylic acids or metal salts of carboxylic acids.
5. The composition of claim 1 wherein (D) is selected from the group consisting of aliphatic hydrocarbons, glycol ethers, esters, alcohols, ester alcohols, ketones, kerosenes, naphthas, petrolatums, carboxylic acids having at least six carbon atoms and amines having at least nine carbon atoms.
6. The composition of claim 1 wherein the mixture of step (I) further comprises a rare earth metal salt of a fatty acid.
7. The composition of claim 1 wherein the mixture of step (I) further comprises a solvent having a boiling point of less than 200°C.
8. The composition of claim 1 wherein (E) is selected from benzoyl peroxide, dichlorobenzoyl peroxide, azobisisobutyronitrile or 2,4-dimethyl-4-methoxyvaleronitrile.
9. The composition of claim 1 wherein step (I) comprises reacting a mixture comprising components (A), (B) and (C), (II) adding components (D) to the product of (I), and optionally (III) heating the product of (II) to form a reaction product.
10. An article of manufacture obtainable by a method comprising:
- (I) applying a silicone pressure sensitive adhesive composition to at least one surface of a substrate, wherein the silicone pressure sensitive adhesive composition is obtainable by the method of any of claims 1 - 10 and
- (II) heating the silicone pressure sensitive adhesive composition and the substrate to cure the composition.
11. The article of manufacture of claim 10 wherein the article is further obtained by (III) contacting a solid support with the substrate having the adhesive composition cured thereon after step (II) whereby the solid support and the substrate are adhered together.



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(54) **Silicone pressure sensitive adhesive compositions**

(57) This invention provides pressure sensitive adhesive compositions which are obtainable by a method comprising reacting a mixture of at least one polydiorganosiloxane, at least one silicone resin copolymer, at least one silanol condensation catalyst, and at least one solvent or plasticizer having a boiling point of at least 200°C., to form a reaction product and then adding an organic peroxide or azo compound to the resultant reaction product. The silicone pressure sensitive adhesives of this invention are useful in preparing articles such as pressure sensitive tapes, labels emblems and other decorative or informational signs.

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EUROPEAN SEARCH REPORT

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Place of search BERLIN		Date of completion of the search 9 November 1999	Examiner HOEPFNER W.
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